

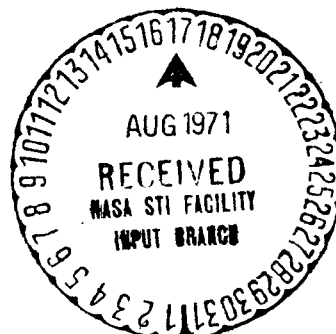
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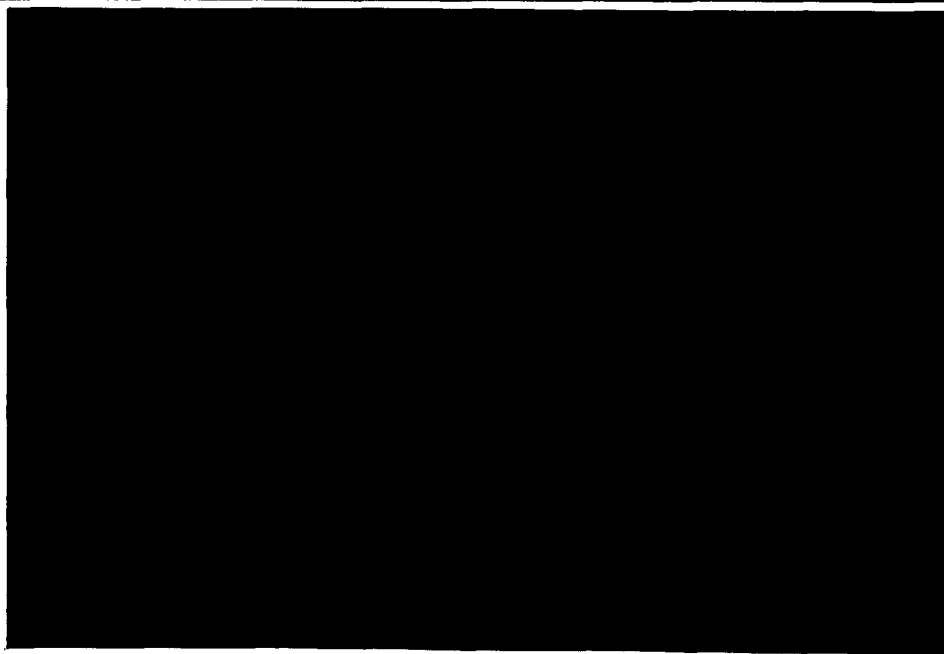
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ORGANIC CHEMISTRY: PRELIMINARY FINDINGS
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EXPERIMENTAL INTERSTELLAR ORGANIC CHEMISTRY:
PRELIMINARY FINDINGS

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ABSTRACT

In a simulation of interstellar organic chemistry in dense interstellar clouds or on grain surfaces, formaldehyde, water vapor, ammonia and ethane are deposited on a quartz cold finger and ultraviolet-irradiated in high vacuum at 77K. The HCHO photolytic pathway which produces an aldehyde radical and a superthermal hydrogen atom initiates solid phase chain reactions leading to a range of new compounds, including methanol, ethanol, acetaldehyde, acetonitrile, acetone, methyl formate, and possibly formic acid. Higher nitriles are anticipated. Genetic relations among these interstellar organic molecules (e.g., the Cannizzaro and Tischenko reactions) must exist. Some of them, rather than being synthesized from smaller molecules, may be degradation products of larger organic molecules, such as hexamethylenetetramine, which are candidate constituents of the interstellar grains. The experiments reported here may also be relevant to cometary chemistry.

In experimental simulations of Jovian atmospheric chemistry, a mixture of the cosmically most abundant fully saturated hydrides -- H_2 , CH_4 , NH_3 , H_2O -- was subjected to electrical discharge; the primary gas phase products produced were the hydrocarbons, acetylene, ethylene and ethane; the nitriles, hydrogen cyanide, and acetonitrile; and the aldehydes, formaldehyde and acetaldehyde (Sagan and Miller, 1960). Computer experiments on quenched thermodynamic equilibrium in similar mixtures of gases produced just this same array of gases as principal products, along with CO (Sagan et al., 1967; Lippincott et al., 1967). The discovery of HCN and HCHO in the interstellar medium prompted the suggestion (Sagan, 1970; Sagan and Khare, 1970) that such experiments may be of relevance to the emerging field of interstellar organic chemistry. The recent announcement of the probable detection of CH_3CN in the interstellar medium (Solomon, Penzias, Wilson, and Jefferts, in press) makes this suggestion more attractive, and has led us to attempt an explicit experimental simulation of interstellar organic chemistry.

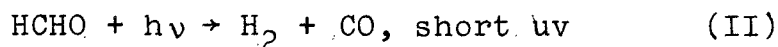
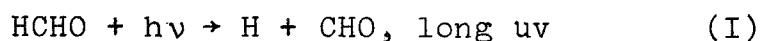
An accurate laboratory simulation of average interstellar conditions is impractical. To employ simultaneously nontrivial uv optical depths as well as mean interstellar densities, laboratories of interstellar dimensions are required. It seems clear that to synthesize polyatomic organic molecules three-body reactions must be invoked, reactions which are unlikely in the extreme under average interstellar conditions. Typical three-body reaction rate constants are $\sim 10^{-32} \text{ cm}^6 \text{ sec}^{-1}$, implying reactant densities $> 10^8 \text{ cm}^{-3}$ for reaction rates to be com-

petitive with typical interstellar uv photodissociation rates (Sagan, 1971). It follows that interstellar organic chemistry does not occur in gas phase under mean interstellar conditions. At least two alternatives may be suggested (cf. Sagan, 1971): in dense clouds with the product molecules perhaps subsequently ejected by radiation and proton pressure after nearby star formation; and in the close vicinity of interstellar grains. Making a virtue of a necessity, we have not hesitated to employ laboratory high vacuums in interstellar simulation experiments.

The experiment is a low-temperature high-vacuum uv irradiation of condensed simple gases known or suspected to be present in the interstellar medium. Because of the discovery of 10μ silicate reststrahlen bands (Stein and Gillett, 1969; Hackwell et al., 1970) and the microwave line identification of SiO (Wilson, et al., 1971) the most appropriate matrix for the condensed gases seems to be a silicate glass. To perform organic chemistry, precursor gases containing H, C, N, and O are required. The molecules chosen were water, ammonia, formaldehyde and ethane. The first three are obvious choices because of their high microwave abundances. Simple hydrocarbons are not accessible to microwave line techniques, although there is every reason to expect their abundant presence in the interstellar medium. Ethane rather than methane was chosen, for experimental convenience and because our experience indicates that in similar experiments it is a useful source of methyl radicals. Ethane is the principal hydrocarbon product from the irradiation of methane under usual laboratory conditions.

The bulk of the interstellar electromagnetic energy density lies longward of 2000 \AA ; yet most of the identified and suspected interstellar molecules are transparent at these wavelengths. Formaldehyde is an important exception, exhibiting a characteristic absorption band between 2300 and 3400 \AA , probably arising from the transition to an antibonding π orbital of the carbonyl group of a non-bonding $2p$ electron of the oxygen atom. The H-CHO bond has an energy of about 3.8 e.v. Thus irradiation at, say, 2537 \AA will produce "hot" hydrogen atoms, superthermal by about 1.1 e.v. (By momentum conservation almost all of the excess energy is acquired by the H atom.) Comparable hot H atoms from the photodecomposition of H_2S are known to initiate chain reactions leading to quite complex organic molecules (Sagan and Khare, 1971a; 1971b).

At room temperature the HCHO photolytic products are wavelength-dependent:



These two pathways have approximately equal probabilities at $\lambda \sim 2600 \text{ \AA}$ (Calvert and Pitts, 1966, pp. 370-371). Although the photolytic pathway may be a sensitive function of the vibrationally excited singlet or triplet state formed, these room temperature results were the only guides available on wavelength choice. A 200-watt Hanovia quartz high pressure mercury vapor lamp, emitting 1.1 watt in the 2537 \AA Hg resonance line was employed. The Hg emission spectrum is relatively rich

in lines to longer wavelengths; the emission spectrum and the Schumann-Runge absorption by atmospheric O_2 in the light path (but not in the reaction vessel) guarantee negligible irradiation below about 2200 Å.

The experimental apparatus is displayed schematically in Figure 1. The gases are frozen at a conveniently low temperature -- here 77K -- on a uv-transparent spectro-sil quartz cold finger in a high-vacuum system. Successive layers of the formaldehyde polymer paraformaldehyde, water, ethane, and ammonia were introduced into the reaction vessel. Initial gases of high purity were used -- as, e.g., Matheson research grade ethane, containing a maximum of 60 ppm CH_4 . $HCHO$ and NH_3 were separated, to inhibit the formation of hexamethylene-tetramine -- a molecule which is nevertheless of interest in interstellar organic chemistry and which is referred to below. The amounts of material introduced were: paraformaldehyde, 2.3 g; H_2O , 0.19 cm³ room temperature liquid equivalent; ethane, 687 cm³ and ammonia, 690 cm³. Access of vacuum system Hg to the reaction vessel was prevented by a spiral trap maintained at -78°C. After deposition and pumping at a pressure $\lesssim 10^{-5}$ torr with a high performance mercury diffusion pump, the layered frosts were irradiated for three hours.

At the end of the experiment roughly 30 cm³ of noncondensable gases produced during the photolysis were detected manometrically, and analyzed with a Perkin-Elmer Model 621 double beam spectrophotometer, revealing the presence of CH_4 and CO. The noncondensable gases were also examined with

an AEI MS 902 double focussing mass spectrometer, which confirmed the presence of methane and carbon monoxide, and also revealed the production of H_2 . Experimentally matching the strengths of the infrared bands, we find approximately 96% of the noncondensable gas to be CO, and approximately 3.9% to be CH_4 . Assuming no other condensable gases to be present, we deduce about 0.1% H_2 . By summing the appropriate mass peaks of the mass spectrum, we find, independently, about 97% CO, 3% CH_4 , and 0.2% H_2 , in good agreement with the infrared results. The production of CO and H_2 are expected from Pathway II of the formaldehyde photolysis. The $[H_2]/[CH_4]$ ratio $\sim 5\%$ is much larger than the ratio $\sim 0.1\%$ expected from cracking CH_4 ; because the system was pumped before irradiation, the H_2 found here cannot be a contaminant in the initial constituents. We attribute the great departure from $[H_2]/[CO] \sim 1$, expected from Pathway II, to reaction of H_2 to form other constituents.

The detection of CH_4 is an important result. Its abundance was more than two orders of magnitude above background. It can only have been produced by a chain reaction initiated through Pathway I, probably by superthermal H atoms. There are several possible pathways to methane, including collisional decomposition of ethane, followed by the recombination of hydrogen atoms and methyl radicals, or the formation and subsequent photolysis of acetaldehyde. The presence of CH_4 demonstrates the mobility of radicals in such irradiated frosts at 77K, and suggests the formation of a variety of other compounds which remain condensed out at 77K.

Accordingly the photolytic products were gradually warmed to -37°C . The temperatures were monitored by Cu-constantan thermocouple in thermal contact with the deposited frosts. The radiation products were then divided into two fractions. The first fraction was transferred again to a 77°K trap and samples successively stored in five receptacles at -196°C , -160°C , -126°C , -111°C and -78°C . Because of diffusion limitations in the gas handling apparatus this represents only a zeroth order fractional distillation. No samples in the first fraction had access to liquid water at any time. The remaining fraction of irradiated products was gradually warmed to room temperature, where a small quantity of liquid water condensed out in the access tube at the bottom of the reaction vessel (Figure 1). Even for this fraction we believe it unlikely that gas phase chemistry was significantly affected by liquid water.

The various samples were examined with a Hewlett-Packard Model 5750 gas chromatograph, and with a Perkin-Elmer Model 270 mass spectrometer/gas chromatograph. With the latter instrument ~ 1000 individual mass spectra of gas chromatographic elution peaks of the various samples were obtained and examined. Typical gas chromatograms, with peaks identified by gas chromatographic techniques alone, are represented in Figure 2. Typical GC programs are given in the figure legend.

The principal molecules identified, with the corresponding analytic technique(s), are exhibited in Table 1. Each of the compounds determined mass spectrometrically corresponds to a gas chromatographic peak on the GC/MS, but here GC is a separation technique, not a detection technique. Table 1 lists gas chromatography as a detection technique only when compounds are independently recognizable by their retention time characteristics. A number of results, such as a larger $\text{CH}_3\text{OH}/\text{C}_2\text{H}_5\text{OH}$ ratio at -111C than at -78C are consistent with the relative vapor pressures of the compounds. We attribute the larger yield of organic molecules in the fraction which was allowed to come to room temperature to the low vapor pressures of these compounds at -37C, preventing their substantial transfer to other low temperature baths. Control samples revealed none of the compounds listed in Table 1.

The production of methanol, acetonitrile, and possibly formic acid are of interest, because these molecules have been reported in the interstellar medium by microwave line

radioastronomy techniques. Although other reaction pathways are possible, the production of methanol and possibly formic acid in this experiment suggests a surface-catalyzed (or gas phase) ultraviolet-induced Cannizzaro reaction, $2\text{HCHO} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{OH} + \text{HCOOH}$. Methyl formate is probably produced by a Tischenko reaction, $2\text{HCHO} \rightarrow \text{CH}_3\text{OOCH}$. A set of unidentified peaks exists in the gas chromatograms (Figures 2). Some but not all of these correspond to compounds identified in GC/MS. The unidentified compounds having larger retention times are all of higher molecular weight than those identified. A variety of unidentified molecules also exist in the GC/MS mass spectra. Only two of the most prominent of these are given in Table 1. Molecule X has cracking pattern peaks at $m/e = 55, 57, 70$, and 71 . Molecule Y has peaks at $m/e = 73, 83$, and 85 . Work on the identification of these gas phase unknowns of high vapor pressure and high molecular weight is continuing.

The suggestion (Sagan, 1970; Sagan and Khare, 1970) that acetonitrile might, on the basis of laboratory experiments, be present in the interstellar medium seems to be supported by the most recent observational evidence (Solomon, et al., 1971). From the present experiments, we suggest searches for acetaldehyde, acetone, ethanol, and methyl formate. The presence of acetonitrile in these experiments strongly implies the production of HCN; and acetylene suggests the presence of ethylene, although, because of masking, such molecules have not been detected directly. The synthesis of amino acids in related experiments (Sagan and Khare, 1971a), probably formed by a Strecker synthesis, suggests that

higher nitriles and, in particular, the nitriles of the simpler amino acids should be suitable targets for further microwave line searches. Because of their very low vapor pressures, the absorption frequencies of the amino acids themselves are difficult to determine.

One implication of this work is that some of the more complex organic molecules discovered in the interstellar medium may be genetically related -- as, e.g., by the Cannizzaro and Tischenko reactions. This implies that the cross-correlation of molecular species in the same cloud may eventually provide a powerful method for verifying proposed reaction schemes. The fact that molecules such as acetone and the aldehydes are very uv-labile, while compounds such as CO are very uv-stable, must of course be taken into account in such correlation attempts.

In the course of experiments preparatory to the one reported here (Sagan and Khare, 1970) the ease of formation of hexamethylenetetramine (HMTA) was brought dramatically to our attention. This compound forms stoichiometrically from formaldehyde and ammonia, $6\text{HCHO} + 4\text{NH}_3 \rightarrow \text{C}_6\text{H}_{12}\text{N}_4 + 6\text{H}_2\text{O}$. HMTA is a colorless solid with a melting point $> 500^\circ\text{K}$. Its high melting point is associated with a symmetry and rigidity of its cage structure. It was the first organic compound to have its structure determined by X-ray diffraction. We calculate that in dense clouds HMTA can form stoichiometrically by collision in times short compared with the formaldehyde photodissociation time, allowing for the ultraviolet extinction within such a cloud. Molecules of this sort have a

marked absorption feature in the vicinity of $2000\overset{\circ}{\text{A}}$; and because of their stability commend themselves as candidate constituents of the interstellar grains.

We are pursuing the photochemistry of HMTA and related compounds, in the expectation that some of the molecules recently detected in the interstellar medium may be photolytic fragments of larger organic molecules rather than the interaction products of smaller molecules (Sagan, 1971). Work is also being pursued in this laboratory on experiments like those reported here, but in which the product analysis is done exclusively at low temperatures -- e.g., by time-dependent infrared spectroscopy of mixed frosts deposited and irradiated on CsI windows.

A remarkable similarity exists between the mass spectrometric cracking patterns of interstellar molecules identified at microwave frequencies, and the radicals in cometary tails identified at optical frequencies (Sagan, 1971). In the expectation that comets are composed at least in part of cosmically abundant ices (Whipple, 1963) and have been uv-irradiated during their history, we propose that experiments of the sort reported here are also of relevance to cometary chemistry.

Acknowledgements: We are grateful to Jeremy Hribar, Francois Raulin, Dennis Ward, Mohan Khare and Lawrence Wasserman for technical assistance, and are particularly indebted to Leon H. Hinman for glassblowing of high excellence. This research was supported in part by NASA Grant NGR 33-010-101.

TABLE 1

Synthesized Molecules at -196°C uv irradiation of $(\text{HCHO})_n$,
 H_2O , C_2H_6 , and NH_3

<u>MOLECULE</u>	<u>DETECTION TECHNIQUE</u>
Fraction collected at -111°C	
methanol, CH_3OH	GC, MS
ethanol, $\text{C}_2\text{H}_5\text{OH}$	GC
acetone, CH_3COCH_3	MS
acetylene, C_2H_2	GC
acetonitrile, CH_3CN ?	GC
Molecule X	MS
Molecule Y	MS
Fraction collected at -78°C	
methanol, CH_3OH	GC, MS
ethanol, $\text{C}_2\text{H}_5\text{OH}$	GC, MS
acetone, CH_3COCH_3	MS
acetylene, C_2H_2	GC
acetonitrile, CH_3CN ?	GC
Molecule X	MS
Molecule Y	MS
Fraction collected at room temperature	
methanol, CH_3OH	GC, MS, IR
ethanol, $\text{C}_2\text{H}_5\text{OH}$	GC, MS
acetone, CH_3COCH_3	MS

TABLE 1
continued

<u>MOLECULE</u>	<u>DETECTION TECHNIQUE</u>
Fraction collected at room temperature	
acetonitrile, CH_3CN	GC, MS
acetaldehyde, CH_3CHO	MS
methyl formate, CH_3OOCH	MS
formic acid, HCOOH ?	MS
Molecule X	MS
Molecule Y	MS

GC = gas chromatography

MS = combined gas chromatography/mass spectrometry

IR = infrared spectroscopy

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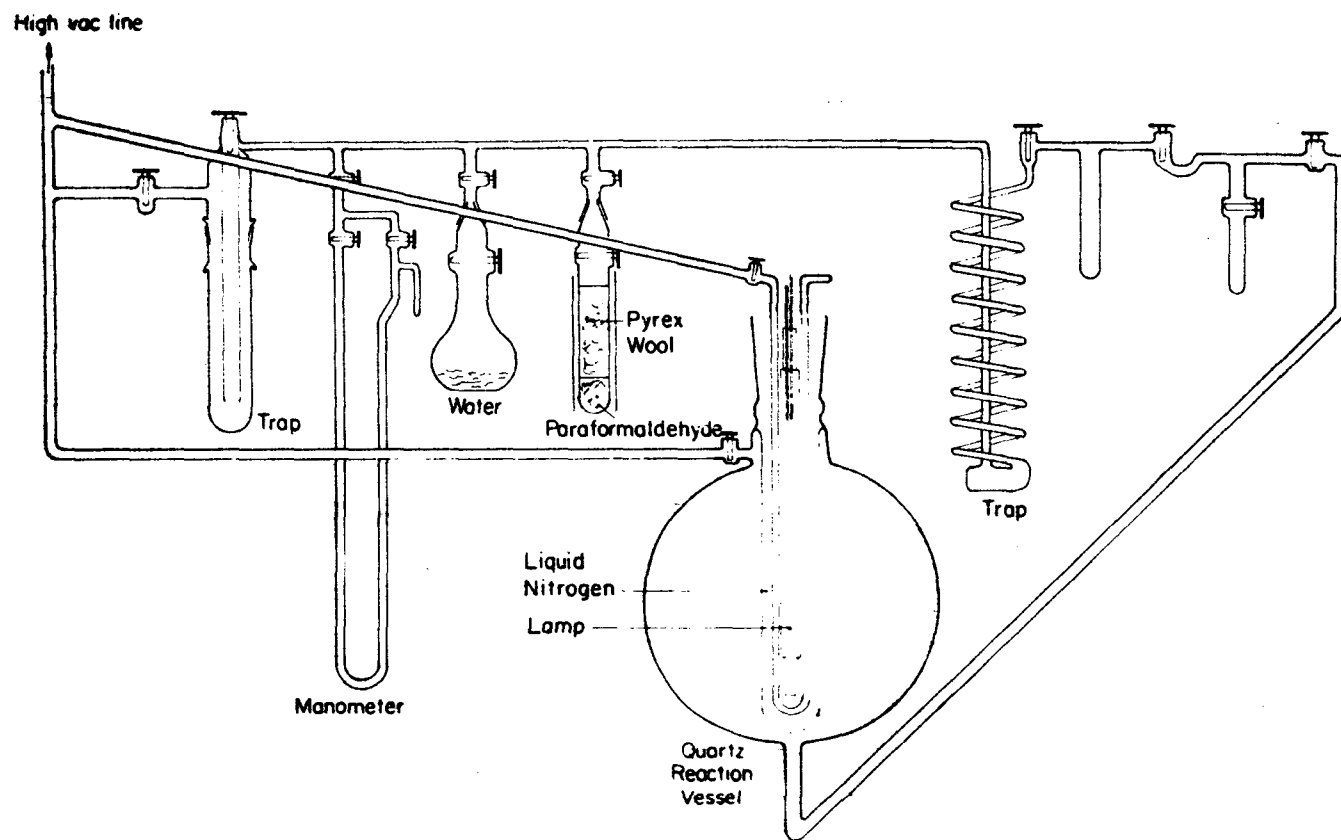
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FIGURE CAPTIONS

Figure 1: Schematic diagram of the experimental apparatus.

Ethane and ammonia, and water and formaldehyde from condensed phases, are introduced into the liquid-N₂ cooled cold finger within the reaction vessel. Frosts deposited on the quartz finger are uv-irradiated in cylindrical geometry from within, under high vacuum.

Figure 2: Representative gas chromatograms of irradiation products raised to -37C and then collected at -79C and -111C. Several of the numbered peaks were subsequently identified by GC/MS.



SYSTEMATIC SKETCH OF THE PHOTOLYSIS APPARATUS FOR LOW TEMPERATURE

Figure 1.

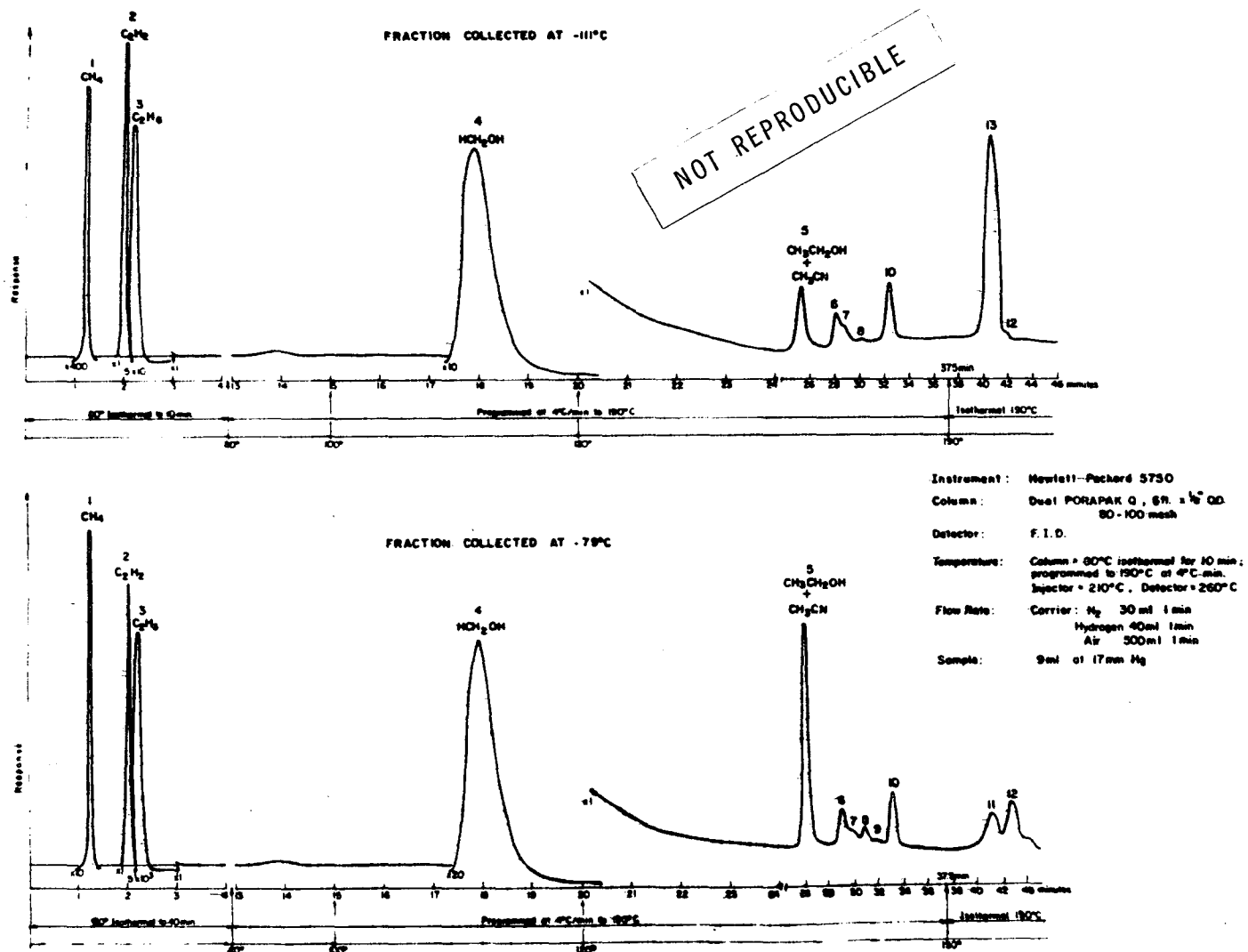


Figure 2.